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Geochemical behaviour of rare earth elements in mining environments under non-acidic conditions

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Abstract

The rare earth elements (REE) were determined in water and solid samples at the abandoned mine of Ingurtosu (Sardinia, Italy). Research was performed to evaluate the main factors that control the geochemical behaviour of REE in near-neutral pH mining environments. REE show the highest concentrations (13-100 µg/l) in drainages from mine tailings, especially when water sampling was carried out under high flow conditions. Positive correlations between ΣREE and Zn and Pb were observed, possibly indicating REE sorption on Zn- and Pb-rich fine particles (<0.4 µm). Fractionation processes were observed normalizing REE in waters with respect to REE in mining-related residues. The Naracauli waters show an enrichment in HREE, probably due to the high stability of dissolved HREE$(CO_3)^{2-}$ complexes in the studied waters. REE fractionation was not observed during hydrozincite bioprecipitation.

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Keywords: REE, stream water, mining wastes, abandoned mine.

1. Introduction and study area

Geochemistry of the rare earth elements (REE) in mining environments has been investigated under acidic conditions (e.g. [1], [2], [3], [4]), while studies under non-acidic pH conditions are less common. In this study, the determination of REE in waters and solid materials in the abandoned mining area of Ingurtosu (Sardinia, Italy) was carried out. The aim was to identify the main factors that control the geochemical behaviour of REE in near-neutral mining environments.

The Ingurtosu Pb-Zn deposit was exploited for about a century until 1968. Main ore minerals were galena and sphalerite, with small amounts of chalcopyrite and pyrite. Mining residues were abandoned on site, resulting in metal dispersion in both soils and waters. Seasonal bioprecipitation of hydrozincite, $Zn_5(CO_3)_2(OH)_6$, allows Zn, Pb, Cd, Cu and Ni attenuation in the Naracauli stream waters (see [5], [6],

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[7] and references therein) .

2. Materials and methods

Fig. 1 shows locations of sampling stations. Water samples include the Naracauli stream (NS-100 to NS-590, which numbers indicate metric distance from station A), and drainages from tailings. Temperature, pH, redox potential (Eh), electrical conductivity (EC), and alkalinity were measured on site. Water was filtered (0.4 μm), and acidified to 1% HNO_3 for analyses by ICP-OES and ICP-MS. REE were determined by ICP-MS and Apex-Q [8]. Anions were determined by ion chromatography in non-acidified aliquots. Speciation calculations were carried out by PHREEQC using the llnl database [9].

Solid samples consist of mining-related residues (MRR) and hydrozincite (HDZ). Mineralogical characterization was determined by X-ray diffraction (XRD), and elemental composition by ICP-OES and ICP-MS following microwave digestion.

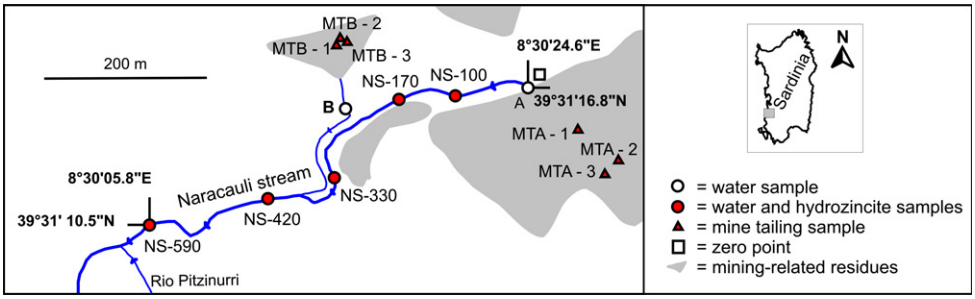

Fig. 1. Map showing the distribution of mining-related residues, and the location of water and solid samples.

3. Results and discussion

The waters show pH values in the range of 6.2 to 8.4, the lowest values being observed in drainages from tailings (6.2-7.0). Eh values (0.40 to 0.52 V) indicate oxidizing conditions. Salinity in drainages from tailings is higher (1.2-2.8 g/l TDS, total dissolved solids) than values in the Naracauli stream (0.6 and 1.6 g/l TDS). Waters have dominant Ca-Mg-SO_4 composition in the Naracauli stream, and Zn-SO_4 in waters flowing out of tailings. Dissolved Zn concentrations attain hundreds mg/l, and Cd and Pb thousands μg/l, with maximum values observed in the waters draining mine wastes.

The MRR samples are mainly composed of quartz, gypsum, sphalerite and phyllosilicates. Dominant metals are Fe and Zn (mean concentrations: 27 g/kg and 21 g/kg, respectively). The hydrozincite contains 500 g/kg Zn, 1200 mg/kg Pb, 700mg/kg Cd and 800 mg/kg Ni.

In the Naracauli stream, ΣREE varies from <0.1 to 9 μg/l, with values decreasing downstream. At the water stations A and B (Fig. 1), ΣREE varies between 13 and 100 μg/l. The highest contents were measured in waters collected under high flow conditions. The ΣREE are correlated with Zn and Pb concentrations, possibly suggesting REE sorption on Zn- and Pb-rich fine particles (i.e. <0.4 μm). The $REE(CO_3)^+$ and $REE(CO_3)^{2-}$ complexes are the prevalent species in the Naracauli stream waters. At stations A and B, characterized by lower pH values and higher sulphate contents, the $REE(SO_4)^+$ species (up to 70 %) and the free-ion REE^{3+} (up to 60 %) occur.

The REE content varies between 20 and 300 mg/kg in MRR solids, and between 5 and 28 mg/kg in hydrozincite samples. Elements La, Ce and Nd are the most abundant REE both in mining wastes and hydrozincite samples (Table 1). Figure 2a shows the mean concentration of each REE in the MRR, in hydrozincite, and in water samples normalized to the corresponding concentration in the Post-Archean

average Australian Shale (PAAS; [10]).

Table 1. Mean (X) and standard deviation (σ) values of REE in water and solid samples; n refers to the number of samples.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
NS-100 to 590														
X (n=107) µg/l	0.28	0.13	0.04	0.1	0.03	0.01	0.03	0.005	0.02	0.006	0.011	0.002	0.008	0.002
σ	0.57	0.24	0.08	0.23	0.04	0.02	0.06	0.007	0.03	0.006	0.014	0.002	0.008	0.001
Stations A and B														
X (n=18) µg/l	24	11	2.6	9	1.5	0.5	2	0.3	1.1	0.2	0.5	0.05	0.2	0.04
σ	13	5.1	1.6	6	0.9	0.38	1.5	0.17	0.75	0.14	0.31	0.03	0.17	0.03
MRR														
X (n=6) mg/kg	20	40	4	20	3	1	3	0.3	1	0.2	0.6	0.07	0.5	0.06
σ	27	45	5	18	3	1	3	0.2	1	0.2	0.4	0.04	0.3	0.04
HDZ														
X(n=6) mg/kg	4.2	2.6	0.5	2	0.4	0.1	0.5	0.07	0.3	0.07	0.2	0.02	0.1	0.02
σ	2.8	2.9	0.4	1.6	0.3	0.1	0.4	0.04	0.2	0.04	0.1	0.01	0.1	0.01

The MRR materials are enriched in LREE relative to the HREE (La_n/Lu_n = 1.9 to 6.6). These patterns also show a slight positive Eu anomaly (Fig. 2a), probably due to the presence of Eu-enriched minerals, such as Ca-feldspar, calcite [11] and sulphide [12]. Hydrozincite shows a slight negative Ce anomaly.

PAAS-normalized patterns of water samples are characterized by a negative Ce anomaly, which is more marked in the Naracauli waters (Fig. 2a). Also, an enrichment in LREE relative to the HREE (La_n/Lu_n = 2.3-12) can be observed. PAAS-normalized REE patterns in waters do not change significantly under different seasonal conditions.

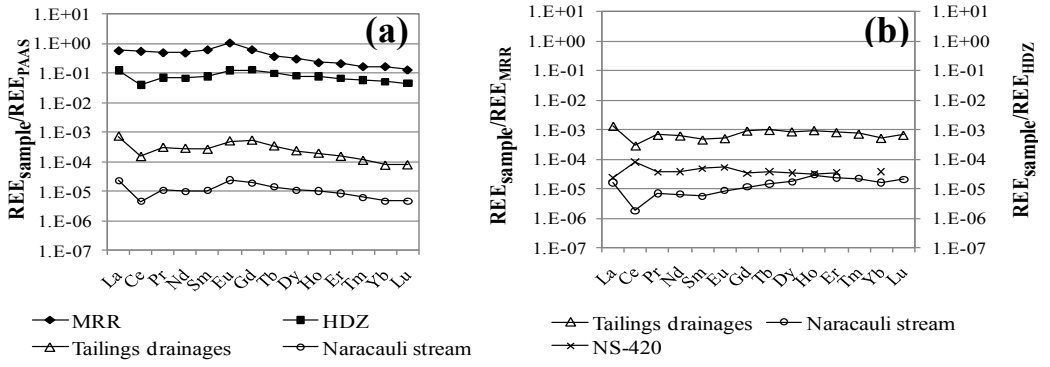

Fig. 2. a) REE patterns of mining-related residues (MRR), hydrozincite (HDZ), tailings drainages, and Naracauli stream waters normalized to the Post-Archean average Australian Shale (PAAS). b) REE patterns of tailing drainages and Naracauli stream waters normalized to MRR, and the Naracauli stream NS-420 normalized to hydrozincite samples collected at the same site.

MRR-normalized REE patterns of water samples are characterized by a negative Ce anomaly (Fig. 2b), also observed in PAAS-normalized patterns (Fig. 2a). The Ce anomaly might result from poor solubility of Ce(IV) species under the observed oxic conditions [13]. Moreover, the Naracauli patterns are characterized by a nearly continuous increase from Sm and Lu. This behaviour suggests that the REE might be fractionated during mine waste alteration/oxidation and subsequent transport. In particular, HREE enrichment could be due to the high stability of $HREE(CO_3)^{2-}$ complexes [13], which dominate in the Naracauli waters.

When the REE in Naracauli stream waters are normalized to REE in hydrozincites collected at the same site (Fig. 2b), patterns show a positive Ce anomaly, which is consistent with the negative Ce anomaly observed in hydrozincites (Fig. 2a).

4. Conclusion

REE geochemistry under non-acidic pH conditions was investigated in the Ingurtosu mining district. REE show the highest concentrations in mine tailings drainages collected under high flow conditions, likely due to higher amounts of REE associated with particles <0.4 μm. Considering MRR normalized patterns, an enrichment in HREE was observed in Naracauli stream waters, likely due to high stability of the $HREE(CO_3)^{2-}$ complexes in solution. Observed Ce negative anomaly in waters could be due to the oxidation of Ce(III) to Ce(IV) that results in Ce immobilization in secondary phase. This work shows that REE have higher affinity to hydrozincite than waters. This could be due to co-precipitation processes and/or adsorption reactions, with the exception of Ce that shows low affinity versus hydrozincite.

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